Growth and electrical properties of N,N[sup]-bis(n-pentyl)terrylene- 3,4:11,12-tetracarboximide thin films

Matthieu Petit, Ryoma Hayakawa, Yasuhiro Shirai, Yutaka Wakayama, Jonathan P. Hill, Katsuhiko Ariga, Toyohiro Chikyow

Growth and electrical properties of *N,N'*-Bis(*n*-pentyl)terrylene-3,4:11,12-tetracarboximide thin films

Matthieu Petit

Advanced Electronic Materials Center, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Ryoma Hayakawa

Advanced Electronic Materials Center, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Yasuhiro Shirai

Advanced Electronic Materials Center, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Yutaka Wakayama

Advanced Electronic Materials Center, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Jonathan P. Hill

Supermolecules Group, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Katsuhiko Ariga

Supermolecules Group, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

Toyohiro Chikyow

Advanced Electronic Materials Center, NIMS, 1-1 Namiki, Tsukuba, 305-0044 Japan

A n-type semiconductor molecule *N,N'*-Bis(*n*-pentyl)terrylene-3,4:11,12-tetracarboximide (TTCDI-5C) was synthesized. Theoretical calculations predict several advantages in electrical properties, including large adiabatic electron affinity and small reorganization energy. The molecule was deposited on SiO_2 surfaces and the structure of the resultant thin film was studied. Grain size and thin film cristallinity improve as the temperature increases. Top-contact organic thin film transistors (OFETs) using TTCDI-5C as the semiconductor layer were fabricated using SiO_2 as the gate dielectric. Values of charge carrier mobility up to 7.24×10^{-2} $cm^2V^{-1}s^{-1}$ and

current on/off ratios higher than 10^4 were obtained, demonstrating the potential of TTCD-5C for use in OFETs.

Organic semiconductor molecules have been a focus of considerable research interest during the past decade, since such molecules have demonstrated their potential for application to flat display panels as well as for low-cost and large-area electronics[1,2].

Regarding organic thin film transistors (OFETs), the highest electrical performances have been achieved with pentacene, a p-type semiconductor, for which carrier mobilities as high as 1.5 $cm^2V^{-1}s^{-1}$ have been reported[3-5]. However, there is a lack of n-type semiconductors with performances comparable to p-channel materials. The preparation of both p-channel and n-channel devices would enable the design of complementary circuits using only semiconducting molecular thin films.

Improvement in the performance of an organic transistor requires optimization of several key attributes of the thin films, especially crystallinity, π-orbital overlap and grain boundary structure. A strong coupling exists between the geometric and electronic structures. Molecules for use in organic transistors should:

- have an extensively conjugated π-electronic system since the π and π*-orbitals form delocalized wave functions that support the charge carriers and a high electron affinity regarding n-channel materials to allow efficient electrons injection into the LUMO[5].
- possess excellent qualities in terms of crystal packing and thin film formation. Most organic molecules with an extensive conjugated π-electron system have an edge-to-face configuration due to intermolecular CH-π interactions, and this type of packing hinders intermolecular π-orbital overlap. The most favorable configuration is face-to-face packing with molecules standing perpendicular to the substrate surface to optimize the overlap of π-orbitals, especially for the first monolayers of thin films, since they will act as a channel when used as organic field effect transistors.
- form thin films with maximal grain size to lessen the detrimental effect of carrier scattering at grain boundaries.

Of the n-type semiconductor molecules, the N-alkyl perylene diimides (PTCDI-R) fulfill these expressed requirements. They have been widely studied and have shown carrier mobility as high as 1.3 $cm^2V^{-1}s^{-1}$ under vacuum[6].

We present in this study results regarding the thin film growth of *N,N'*-Bis(*n*-pentyl)terrylene-3,4:11,12-tetracarboximide[7] (TTCDI-5C) (Fig. 1(a)) and the electrical properties of the corresponding thin film field effect transistors.

It was expected that this terrylene derivative molecule would be worthy of attention since the conjugated π- electronic system is more extended than that of the perylene.

At room temperature the transport regime is mainly led by hopping, so that, at the molecular level, charge transport can be described as the exchange of a carrier between a charged molecule and a neutral one. Regarding the semi-classical Marcus theory, the rate for carrier hopping can be written as[5,8]:

$$k = \frac{4\pi^2}{h}\frac{J^2}{\sqrt{4\pi\lambda_B T}}e^{\left(\frac{-\lambda}{4k_B T}\right)} \qquad (1)$$

The two parameters J and λ are the key. J is the transfer integral between two adjacent molecules and must be as large as possible, while λ is the reorganization energy and is related to the geometric relaxation of the charged molecules[9]. λ should be minimized to maximize transport properties.

From calculation at the B3LYP/6-31G(d) level, the respective values of λ and adiabatic electronic affinities (EAa) for PTCDI-R and TTCDI-R are given in Table I and isosurface plots of the frontier orbitals are also shown (cf. Fig. 1(b)). The p-orbitals of oxygen atoms clearly contribute to π-HOMO and π-LUMO. The reorganization energy λ of TTCDI-R is lower and the adiabatic electron affinity (EAa) is larger than that of PTCDI-R. These results are consistent with increased conjugation length. Therefore, the larger electron affinity should lead to a more facile

injection of electrons into the LUMO[9,10] with the smaller λ being advantageous for carrier hopping between molecules.

TTCDI-5C[11-14] thin films were deposited using a vacuum deposition technique with a base pressure below $5x10^{-9}$ Torr. Stable deposition rate and effective delivery of the molecules were thus possible, with the molecules being focused on the substrate through a heated glass tube set between the crucible and substrate[15]. A deposition rate of about 0.1 ML min^{-1}, monitored using a quartz crystal microbalance, was used in all the experiments of this work. n-type Si(001) terminated by SiO_2 layers was used as the substrate throughout.

The structure and morphology of the thin films were examined by atomic force microscopy (AFM SII, SPI4000). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover (Cu Kα source, λ = 0.15418 nm) to check the crystallinity of the thin films.

Thin film field effect transistors based on TTCDI-5C molecules were made using silicon substrates with thermally grown silicon dioxide at a thickness of 214 nm. Top contact configuration was chosen for an FET with 50 nm thick gold electrodes for the drain and source. Electrical properties were investigated using Agilent Technologies B1500A Semiconductor devices analyzer operating under vacuum.

First, the effect of substrate temperature on the morphology and the crystallinity of the thin films was investigated. 15 ML-thick organic thin films were prepared and substrate temperature was varied from room temperature (RT) to 200 °C. AFM images are presented in figures 2(a)-(d). Grain size and shape evolve with temperature. At RT, grains are somewhat circular with diameters of approximately 50 nm. As the temperature is increased, grain shape becomes more rectangular. At 140 °C, grain dimensions reach about 250 × 50 nm. Surface roughness remains in the range 1 – 5 nm over the temperature range RT to 140 °C (cf. Fig. 2(h)). At higher temperatures, surface morphology differs substantially: coverage of the surface by the grains is degraded. Roughness increases dramatically, reaching 14 nm at 200 °C. The critical

temperature in terms of quality of the surface morphology, coverage and roughness appears to be 140 °C.

Next, we studied the formation of the first five monolayers of the organic thin films. This is because the initially formed monolayers act as a channel in the OFET. For this purpose, the substrate temperature was fixed at 140 °C. From the AFM images in figures 2(e)-(g) we can observe that the first two layers completely cover the substrate surface and that growth is two-dimensional. Subsequently, grain-like morphology appears and the three-dimensional growth mode predominates.

Structural analyses of the TTCDI-5C thin films were obtained by using XRD measurements. Typical XRD pattern is shown in figure 3, taken at 140 °C. XRD pattern contains a primary peak labeled (001) at $2\theta = 5.58°$ which corresponds to a *d* spacing of 1.58 nm. This reveals that the molecules stand upright on their alkyl chains at an angle to the substrate surface. We should mentioned that at low substrate deposition temperature, we observed a second peak close to the (001) one at $2\theta = 4.90°$. It was attributed to a metastable thin-film phase as previously reported for pentacene and PTCDI-5C[6,16]. Furthermore the TTCDI-5C thin film exhibits (00*l*) Bragg reflections up to the fourth order. The full width at half maximum (FWHM) of the rocking curve of the (001) peak is $0.12° \pm 0.01°$ (substrate Si(004): 0.04°). This means that the thin film is quite well-ordered, which is a key requirement for efficient charge transport, although this value is slightly higher than that obtained for PTCDI-5C under the same growth conditions (0.06°)[16].

Taken together, the results from AFM images and XRD pattern suggest that the use of a substrate temperature deposition of 140 °C is a good compromise in term of grain size, surface roughness and crystallinity of the thin films. According to these observations, organic thin films transistors were fabricated using this substrate temperature.

Here we present results regarding the properties of organic field effect transistors prepared using TTCDI-5C molecules. Measurements were conducted under low vacuum and

samples were temporarily exposed to air before introduction into the vacuum electrical measurement system. From the I_D-V_D curves in figure 4 inset, these molecules clearly show n-type operation. Figure 4 shows the dependence of the drain current I_D on the gate voltage V_G for a drain voltage of V_D = 70 V. The saturation regime current is given by the following equation[5,18]:

$$I_D = \frac{W}{2L} C_{ox} \mu_{sat} (V_G - V_T)^2 \quad (2)$$

where C_{ox} is the gate dielectric capacitance per unit area, μ_{sat} the field effect mobility at saturation regime and V_T the threshold voltage.

The field effect saturation mobility μ_{sat} was calculated from Equation (2) and the slope $I_D^{1/2}$ vs. V_G in the saturation region. The mobility was found to be 7.24 x 10^{-2} $cm^2V^{-1}s^{-1}$ for a channel length and width of 50 μm and 400 μm respectively. I_{ON}/I_{OFF} ratio was 12200 and the threshold voltage 16 V.

The reason for motilities remaining low may be due to the short air exposure just before the introduction of the sample in the electrical measurement system. These organic anions are easily oxidized by water and oxygen, so that devices quickly cease to operate in air. Currently, experiments using a vacuum transfer system are ongoing for improving device performance.

In summary, theoretical calculations indicate that key parameters, such as the reorganization energy and the adiabatic electron affinity related to the charge transport properties, make TTCDI-5C more suitable than PTCDI-5C for use as the semiconductor in OFETs.

TTCDI-5C thin films were deposited on an SiO_2 surface under vacuum using a hot wall deposition technique. Surface morphology and film structure were analyzed using AFM and XRD. Grain size increases slightly with temperature from 50 nm to 50 × 250 nm at 140 °C. Surface roughness remains in the range 1 to 5 nm up to 140 °C and then increases substantially up to 200 °C. XRD measurements indicate a fairly well-ordered thin film at 140 °C with (00*l*)

Bragg reflections corresponding to a *d* spacing of 1.58 nm. Furthermore, a metastable thin-film phase was detected at lower substrate deposition temperatures.

Organic field effect transistors have been fabricated using TTCDI-5C molecules as the semiconductor thin film in a top-contact configuration. Field effect mobility of 7.24 x 10^{-2} $cm^{2}V^{-1}s^{-1}$ was obtained in the saturation regime. This study demonstrates the potential of the terrylene family of derivatives for the fabrication of OFETs.

References and Notes

1. C.D. Dimitrakopoulos, P.R.L. Malenfant, Adv. Mater., vol. 14, Issue 2, 2002, 99-117
2. G. Horowitz, J. Mater. Res., vol. 19, No. 7, 2004, 1946-1962
3. S.F. Nelson, Y-Y Lin, D.J. Gundlach, T.N. Jackson, Appl. Phys. Lett. 72, 15, 1854-1856
4. C. D. Dimitrakopoulos, D.J. Mascaro, IBM J. RES. & DEV. Vol 45, n 1, Jan 2001
5. C. R. Newman, C.D. Frisbie, D.A da Silva Filho, J-L. Bredas, P.C. Ewbank, K.R. Mann, Chem. Mater. 2004, 16, 4436-4451
6. R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. da Silva Filho, J.-L. Bredas, L. L. Miller, K. R. Mann, C. D. Frisbie, J. Phys. Chem. B.; 2004; 108(50); 19281-19292
7. Synthesis process available in supplementary informations.
8. J. Cornil, D. Beljonne, J-P. Calbert, J-L. Bredas, Adv. Mater. 2001, 13, No14, 1053-1067
9. H.-Y. Chen, I. Chao, Chem. Phys. Lett. 401 (2005) 539-545
10. V. Coropceanu, M. Malagoli, D. A. da Silva Filho, N. E. Gruhn, T. G. Bill, J. L. Bredas, Phys. Rev. Lett. Vol.89, No.27, 275503 (2002)
11. H. Kaiser, J. Lindner, H. Langhals, Chem. Ber. 1991, 124, 529-535.
12. F. Süssmeier, H. Langhals, Eur. J. Org. Chem, 2001, 607-610.
13. a) H. Langhals, F. Süssmeier, J. Prakt. Chem., 1999, 341, 309-311. b) H. Langhals, J. Büttner, P. Blanke, Synthesis, 2005, 3, 364-366.
14. F. Nolde, W. Pisula, S. Müller, C. Kohl, K. Müllen, Chem. Mater., 2006, 18, 3715-3725.
15. H. Sasaki, Y. Wakayama, T. Chikyow, E. Barrena, H. Dosch, K. Kobayashi, Appl. Phys. Lett. 88, 081907 (2006)
16. D. J. Gundlach, T. N. Jackson, D. G. Schlom, S. F. Nelson, Appl. Phys. Lett., 74, Issue 22, pp. 3302-3304 (1999)
17. M. Petit, R. Hayakawa, Y. Wakayama, T. Chikyow, J. Phys. Chem. C, 2007, 111, 12747-12751

18. G. Horowitz, Adv. Mater. 1998, 10, No 5, 365-377

Table I: Reorganization energies (λ), adiabatic electron affinities (EAa) and HOMO-LUMO bandwidth of PTCDI-R and TTCDI-R

	λ (meV)	EAa (eV)	HOMO-LUMO bandwidth (eV)
PTCDI-R	265	2.32	2.54
TTCDI-R	222	2.50	1.99

Table 1.

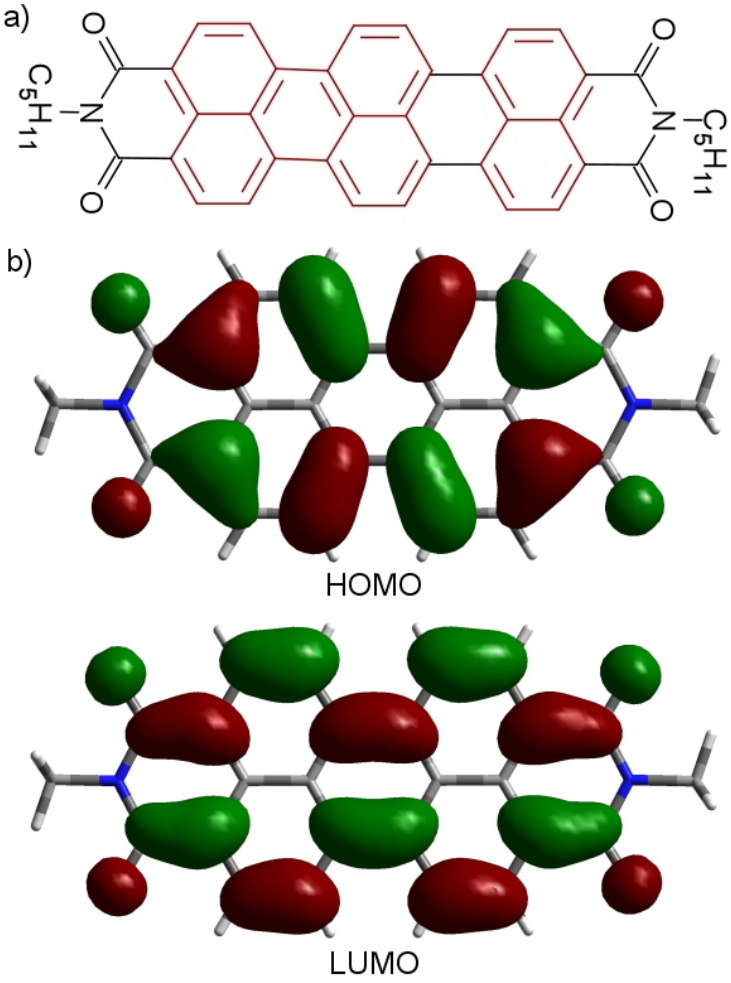
Figures captions

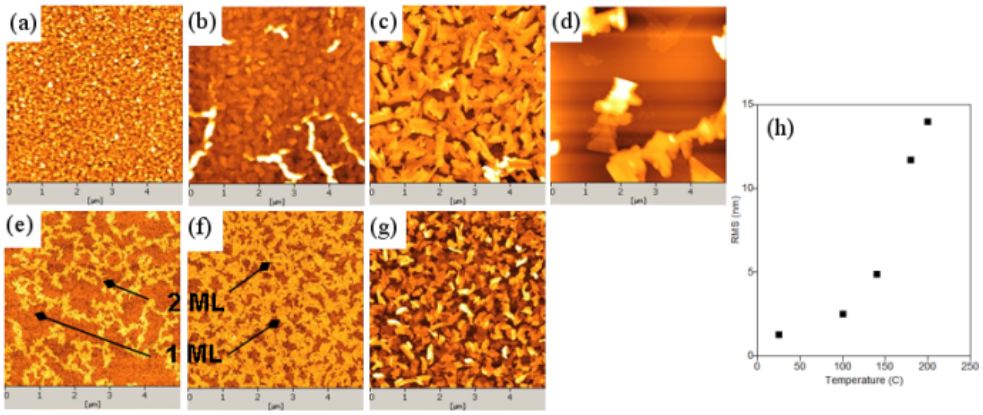
Figure 1: a) Chemical structure of *N,N'*-Bis(*n*-pentyl)terrylene-3,4:11,12-tetracarboximide (TTCDI-5C). b) Isosurface plots of frontier orbitals, including LUMO and HOMO of TTCDI-5C.

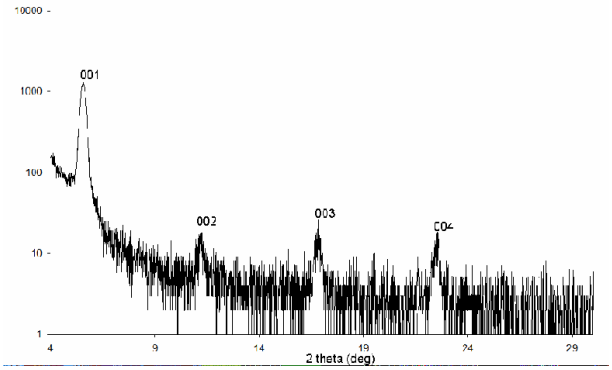
Figure 2: AFM images of TTCDI-5C thin films. (a)-(d): 15 ML, substrate temperatures of RT, 100 °C, 140 °C and 200 °C respectively. (e)-(g): 1.3, 1.6 and 5 ML at 140 °C. h: surface roughness of the 15 ML thick films versus substrate temperature.

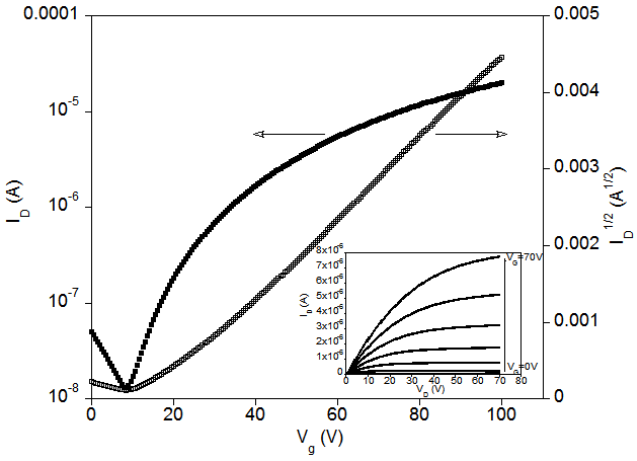
Figure 3: θ-2θ X-ray diffraction scans (logarithmic scale) of TTCDI-5C thin films deposited at 140 °C with a thickness of 30 ML.

Figure 4: Electrical characterization of OFET. $I_D^{1/2}$-V_G curve at V_D = 70 V. Length of the FET channel: 50 μm. Inset: I_D-V_D curves for V_G from 0 to 70 V


a)
O
O
N
C_5H_{11}
O
O
N
C_5H_{11}
b)
HOMO
LUMO


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
2 ML
1 ML
RMS (nm)
Temperature (C)


10000
1000
100
10
1
001
002
003
004
4
9
14
19
24
29
2 theta (deg)


0.0001
10-5
10-6
10-7
10-8
ID (A)
0.005
0.004
0.003
0.002
0.001
0
ID 1/2 (A1/2)
0
20
40
60
80
100
Vg (V)
Vg=70V
Vg=0V
Id (A)
Vd (V)